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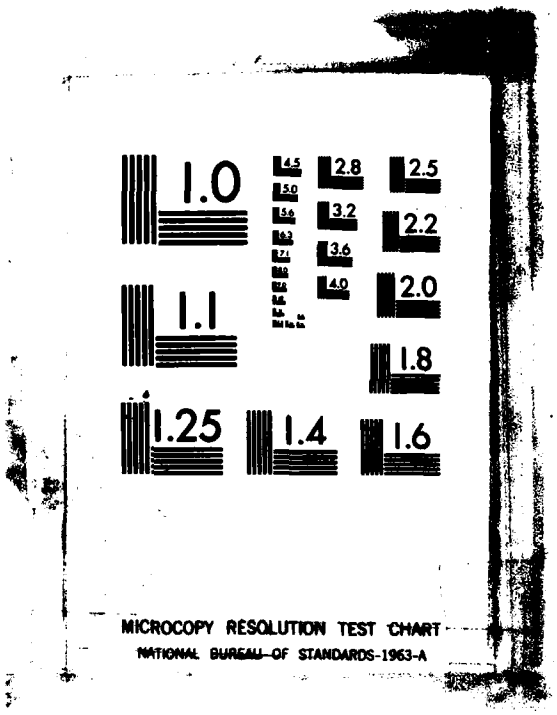
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FINAL REPORT

INNOVATIVE DETECTION, SEPARATION, AND SAMPLING TECHNIQUES FOR TRACE ANALYSIS BY GAS CHROMATOGRAPHY

AFOSR-80-0011

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Microwave heating

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Several studies related to sampling, separation and detection by gas chromatography have been concluded. Fundamental studies and practical applications have been made of selective electron capture sensitization in which the response of an electron capture detector is modified by addition of nitrous oxide to the carrier gas. Sizable signal enhancements have been observed for acetonitrile, acrylonitrile, acrolein, several amines, phenols and polycyclic aromatic hydrocarbons. A selective sorbent has been synthesized and developed that, when used as a chromatographic pre-column, selectively

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removes and concentrates oxygenates from a sample stream that also contains other organic compounds such as hydrocarbons and chlorinated hydrocarbons. A separation of a complex mixture of metal chelates has been accomplished using a bonded-phase, wall-coated fused silica capillary chromatographic column. Limited success has resulted from attempts to separate optical isomers when a chiral metal chelate is incorporated into a chromatographic stationary phase.

Innovative Detection, Separation, and Sampling Techniques for Trace Analysis by Gas Chromatography

The primary objectives of the research originally proposed under Grant No. AFOSR 80-0011 are presented below.

- Continuation of the development and study of selective electron capture sensitization (SECS) as a means to perform highly sensitive measurements of compounds that generally are not amenable to electron capture detection.
- Pre-analysis separation of complex mixtures using a serial sorbent sample collection system
- Studies of chromatographic columns using lanthanide metal chelates including chiral chelates as a means to separate optical isomers.
- Studies of microwave heating in chromatographic systems.

Information in this final report presents the results and conclusions of this research.

Selective Electron Capture Sensitization (SECS)

Additional progress has been made in understanding and eliminating response peculiarities observed with a N_2O-SECS system (1,4,5). Several problems associated with SECS are eliminated by carefully purifying the gases employed in the system. Various gas purifying schemes have been used and a suitable purifying agent has been found that results in reproducable behavior of the system.

Various classes of organic compounds have been studied using SECS. Sizable signal enhancements have been recorded for acetonitrile, acrylonitrile, acrolein, and various amines, phenols, and polycyclic aromatic hydrocarbons (5). The technique was used to aid in the identification of phenolic compounds in a complex wastewater fraction (5). A method for the trace analysis of vinyl chloride has also been developed using SECS (1).

Large differences in response have been found for closely related isomers of amines. These differences could be exploited to positively identify isomers which cannot be identified by other techniques such as mass spectroscopy.

The SECS technique is now being used routinely by other groups. Scientists at the NOAA Aeronomy Laboratory, Boulder, Colorado, our collaborators on the initial development of SECS, use the technique to monitor CO concentrations in ambient air. We have helped Dr. Randolph Ware, a geophysicist colleague at the Cooperative Institute for Research in Environmental Sciences at the University of Colorado, to use SECS to monitor H_2 concentrations in soil gases along earthquake fault zones.

Selective Sorbents

A novel bis(β-diketone), H_2dihed, [p-di(4,4,5,5,6,6,6-heptafluoro-1,3-hexanedionyl)benzene] has been synthesized. This compound has the ability to form coordination polymers with the lanthanides. The polymers retain the excellent Lewis acidity characteristics of previously synthesized fluorinated tris(β-diketonates), yet are extremely non-volatile and consequently more suitable for use as stationary phases in gas chromatography. When incorporated into a pre-analytical column, the polymers were shown to be effective in separating oxygenated compounds from hydrocarbons and chlorinated

hydrocarbons, based upon complexation between the nucleophilic oxygen and the coordinatively unsaturated lanthanide.

The pre-column sorbent was applied to the separation of complex-forming from non-complex-forming solutes in the analysis of volatile organic compounds in wastewater effluent, a fragrance essence, tobacco smoke, urine and gasoline (2,3). In each case a separation into two fractions was accomplished, producing simplified chromatograms. The net result has facilitated identification of organic compounds by mass spectral and retention time matching techniques. Based on these tests with a variety of sample types containing highly complex mixtures, it can be concluded that this is a highly promising general analytical strategy.

Lanthanide β-diketonates have been successfuly bonded to styrene-divinylbenzene copolymers. This sorbent has been characterized and used in the analyses of oxygenated species in the atmosphere. Preliminary experiments have also been performed using N,N-ethylenebis(salicylideniminato)cobalt(II), Co(salen), coated on glass beads. This compound shows selectivity for the retention of Lewis bases containing nitrogen such as pyridine and methylpyridines.

The development of a selective sorbent for olefinic compounds has not been successful. Neither Rh(facam)$(CO)_2$, where facam is trifluoroacetyl-d-camphorate, nor Ag(hfa), where hfa is 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate, retained any of the olefins passed over a bed of the complex that had been dissolved in a liquid phase and coated on a solid support. Many Pd complexes have also been studied. Although olefins can be retarded in the GC analysis, the interaction does not appear to be strong enough to quantitatively trap target compounds for later desorption and analysis. During the course of this study, however, an improved procedure has been discovered for the synthesis of di(o-phenylenebisdimethylarsine)-palladium(II)dichloride and dichloro-o-phenylenebisdimethylarsinepalladium(II).

Chromatography with Metal Chelates

A mixture of synthesized mixed ligand Cr(III) complexes was studied by GC/MS (7). The mixture was made from an equimolar solution of Cr(III), Hhfa (1,1,1,5,5,5-hexafluoro-2,4-pentanedione), Htfa (1,1,1-trifluoro-2,4-pentanedione), and Hfod (2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione). Of the 25 possible products, 24 were resolved using a fused silica capillary GC column. Mass spectrometric detection led to facile assignment of identities of the complexes and yielded information concerning gas phase stabilities.

A number of metal chelates with a new ligand, 2,2,7-trimethyloctane-3,5-dione, Htod, have been investigated for their use in gas and liquid chromatographic separations of transition metals (6). $Cr(tod)_3$ shows extraordinary stability in gas chromatographic columns at temperatures high enough to produce reasonably rapid elution. $Cr(tod)_3$ and $Co(tod)_3$ form geometrical isomers which can be separated on a reversed-phase analytical HPLC column using acetonitrile and water as eluents. $Ni(tod)_2 \cdot MeOH$, $VO(tod)_2$, and $Hg(tod)_2$ have been synthesized and the properties of these new compounds studied. These metal chelates and the isomers of the more stereochemically rigid complexes have been characterized by thermal gravimetric analysis, mass spectrometry, and, in the case of the diamagnetic $Co(tod)_3$, by nuclear magnetic resonance spectrometry. Additionally, the separation of all the geometrical isomers in a mixture of $Cr(tfa)_3$, $Cr(fod)_3$, and $Cr(tod)_3$ was accomplished in a single HPLC experiment.

The symmetrical hexadentate ligand, 1,1,1-tris-(2-oxo-9,9,9-trifluoro-6,8-nonanedione)ethane (H_3tfne), has been synthesized. The synthesis of the Co(II), Co(III), Fe(III), Eu(III) and Yb(III) complexes with H_3tfne has been investigated, but characterization of the cmplexes has proven difficult.

The use of chiral lanthanide metal chelates in gas chromatographic stationary phases has resulted in limited success. A stationary phase containing Eu(III)$(facam)_3$ was able to partially resolve the isomers of epoxypropane.

Microwave Heating in Chromatographic Systems

Several attempts were made to use selective microwave heating in chromatographic systems, with limited success. The first involved the selective heating of a microwave-absorbing liquid phase (TCEP) coated on Chromosorb W. Some changes were seen in the separation of six test compounds, but it has been difficult to regulate and predict the effects of microwave radiation on other chromatographic separations.

Written Publications in Journals and Books

1. "Vinyl Chloride Detection at Sub-ppb Levels Using a Chemically Sensitized Electron Capture Detector", P. D. Goldan, F. C. Fehsenfeld, W. C. Kuster, M. P. Phillips, and R. E. Sievers, Anal. Chem., 52, 1751(1980).

2. "Lanthanide Metal Chelates as Selective Complexing Sorbents for Gas Chromatography", J. E. Picker and R. E. Sievers, J. Chromatogr., 203, 29(1981).

3. "*Applications of* Selective Complexation by a Europium(III) Coordination Polymer Sorbent for the Pre-fractionation of Volatile Compounds", J. E. Picker and R. E. Sievers, J. Chromatogr., 217, 275(1981).

4. "Selective Electron Capture Sensitization", M. P. Phillips, P. D. Golden, F. C. Fehsenfeld, and R. E. Sievers, Chapter in book entitled "Electron Capture - Theory and Practice in Chromatography", Elsevier Publishing Co., 1981.

5. "Selective Electron Capture Sensitizaton of Water, Phenols, Amines and Aromatic and Heterocyclic Compounds", M. A. Wizner, S. Singhawangcha, R. M. Barkley, and R. E. Sievers, J. Chromatogr., 239, 145(1982).

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7. "Gas Chromatography Combined with Mass Spectrometry in Studies of Complex Mixtures of Tris(β-Diketonato)Chromium(III) Geometrical Isomers with Fused Silica Capillary Columns", R. E. Sievers and K. C. Brooks, Int. J. of Mass Spectr. and Ion Physics, 47, 527(1983).

Presentations (Presented by author in **boldface**)

"Selective Sorbents for Chromatography of Environmental Pollutants", **R. E. Sievers**, Tswett Chromatography Medal Award Address, 16th Intl. Symp. on Advances in Chromatography, Barcelona, Spain (Sept. 28, 1981).

"Stereochemistry of Metal β-Diketonates", **R. E. Sievers**, Chemistry Dept. Seminars, Universite de Nice and Universite de Montpelier, France (Oct. 5,6, 1981).

"Lanthanide Chelates as Shift Reagents, Selective Sorbents and Fuel Additives", **R. E. Sievers**, K. C. Brooks, T. J. Wenzel, E. J. Williams, and J. E. Picker, Symposium on Lanthanide Chemistry, Intl. Union of Pure and Applied Chemistry Conference, Vancouver, Canada (Aug. 17, 1981).

"Gas Chromatography Combined with Mass Spectrometry in Studies of Complex Mixtures of Tris(β-Diketonato)Chromium(III) Geometrical Isomers with Fused Silica Capillary Columns", **R. E. Sievers** and K. C. Brooks, Intl. Conference on Mass Spectrometry, Vienna, Austria (Sept. 2, 1982).

"Gas Chromatography Coupled with Mass Spectrometry of Metal Chelates", **R. E. Sievers** and K. C. Brooks, Intl. Conf. on Coordination Chemistry, Budapest, Hungary (Aug. 23, 1982).

"Selective Electron Capture Sensitization", **R. E. Sievers**, M. P. Phillips, F. C. Fehsenfeld, and P. D. Goldan, Chromatography Award Symposium (honoring J. E. Lovelock), 179th National ACS Meeting, Houston, Texas (March 1980).

"Selective Sorbents and Detectors in Chromatography", **R. E. Sievers**, Chemistry Dept. Seminar, Univ. of Arizona, Tuscon, Arizona (November 28, 1979).

"Chromatographic Studies of Environmental Chemistry", **R. E. Sievers**, Chemistry Dept. Seminar, Univ. of Washington, Seattle, Washington (May 1981).

"Environmental Analysis by High Resolution Gas Chromatography Coupled with Mass Spectrometric and Electron Capture Detection", **R. E. Sievers**, S. B. Hawthorne, M. K. Conditt, R. S. Hutte, E. J. Williams, and R. M. Barkley, Hueston Woods Chromatography Symposium, Oxford, OH (June 18, 1982).

"Gas Chromatography and Mass Spectrometry in Environmental Analysis", **R. E. Sievers**, R. M. Barkley, R. S. Hutte, E. J. Williams, M. K. Conditt, and S. B. Hawthorne, Wichita State Univ., Wichita, KA (Dec. 7, 1983).

"Gas Chromatography and Mass Spectrometry in Environmental Analysis", **R. E. Sievers**, R. M. Barkley, R. S. Hutte, E. J. Williams, M. K. Conditt, and S. B. Hawthorne, 39th ACS Southwest Regional Meeting, Tulsa, OK (Dec. 8, 1983).

"Selective Electron Capture Sensitization of Water, Phenols, Amines, and Aromatic and Heterocyclic Compounds", M. A. Wizner, S. Singhawangcha, **R. M. Barkley** and R. E. Sievers, 17th Intl. Symp. on Advances in Chromatography, Las Vegas, Nevada (April 5, 1982).

"Selective Sorption of Nucleophiles Using Lanthanide Metal Complexes", **J. E. Picker** and R. E. Sievers, 180th National ACS Meeting, Las Vegas, Nevada (Aug. 27, 1980).

"Concentration and Measurement of Oxygen-containing Compounds in the Atmosphere", **E. J. Williams**, and R. E. Sievers, 24th Rocky Mtn. Conf. on Analytical Chem., Denver, CO (Aug. 2, 1982).

"Studies of Complex Mixtures of Tris(βdiketonato)chromium(III) Geometrical

Isomers with Fused Silica Capillary Columns", R. E. Sievers and **K. C. Brooks**, 24th Rocky Mtn. Conf. on Analytical Chem., Denver, CO (Aug. 3, 1982).

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J. E. Picker
K. W. Sigvardson
S. W. Stiller
E. J. Williams
M. A. Wizner

Advanced Degrees

The following recieved advanced degrees under partial sponsorship of AFOSR Grant No. 800011:

K. C. Brooks, Ph. D., 1981, "NMR Lanthanide Shift Reagents with Polydentate Cage Ligands and the Gas Chromatographic Separation of Tris(β-diketonato)chromium(III) Geometrical Isomers with Fused Silica Capillary Columns".

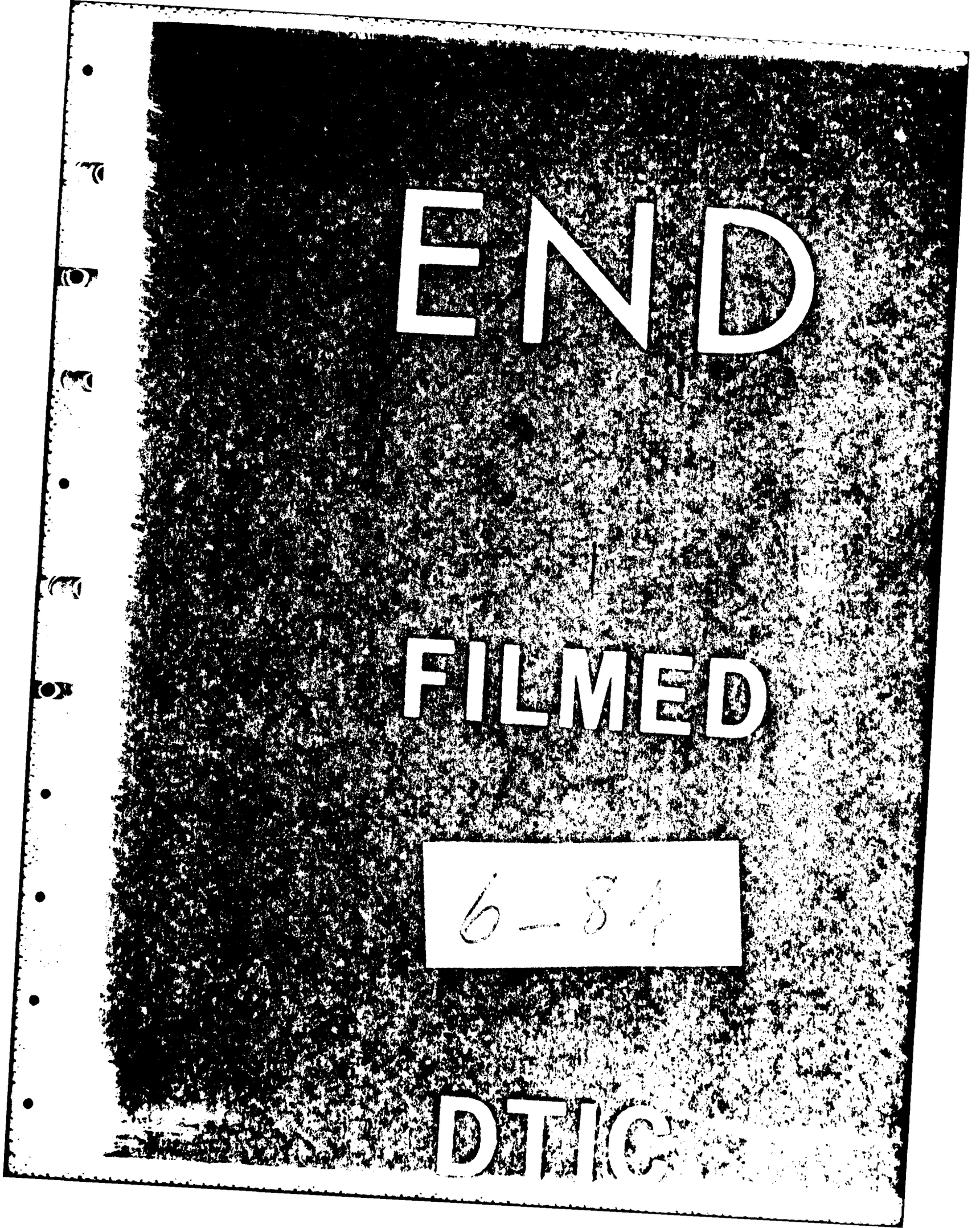
S. D. Harvey, M.B.S., 1981, "Concentration Profile of Volatile Organics in the Atmosphere During a Twenty-four Hour Period".

M. P. Phillips, Ph. D., 1980, "Chemical Sensitization of an Electron Capture Detector to Weakly Electron Attaching Compounds."

J. E. Picker, Ph. D., 1981, "The Use of Lanthanide Chelates as Selective Complexing Sorbents for Gas Chromatography".

E. J. Williams, Ph. D., 1984, "Metal Beta-Diketonate Chelates as Emissions - Reducing Fuel Additives and a Lanthanide Containing Polymeric Selective Sorbent".

M. A. Wizner, Ph. D., 1981, "Determination of Compound Responses to a Sensitized Electron Capture Detector".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